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Introductory remarks

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The inspiring developments in physics, chemistry and astronomy of H_3^+, which led to this Royal Society Discussion Meeting, are summarized.

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1. Discovery

H_3^+ was discovered by J. J. Thomson (1911), who spent most of his research life on studies of the discharges of electricity through gases. He studied negative (cathode) rays and discovered the electron in 1897; he then studied positive (canal) rays, extending Wien's work, and identified the proton. When Aston became his assistant in 1910, an early prototype of a mass spectrometer resulted and H_3^+ was one of the earliest species to be discovered by the apparatus. A plate showing the trace of H_3^+ (Thomson 1912) is shown in figure 1. While he correctly identified in the two papers the signal as being due to H_3^+, he seemed to have had 'discoverer's doubt' as to its identity and he refers to it as X_3 in both editions of his monographs on the positive ray (Thomson 1913, 1921). In his autobiography (Thomson 1937), however, he clearly states 'one of the first things discovered by the photographic method was the existence of H_3^+'.

The younger generation did not have discoverer's doubt and readily accepted H_3^+. Dempster (1916) demonstrated the predominance of H_3^+ over H_2^+ and H^+ in hydrogen plasmas and correctly explained the production of H_3^+ as due to a secondary reaction. Hogness & Lunn (1925) seem to be the first to have written down the celebrated ion–neutral reaction,

$$H_2 + H_2^+ \rightarrow H_3^+ + H. \qquad (1.1)$$

A great many papers have been published on this reaction, and readers are referred to a review (Oka 1983). These works have established the high efficiency of the reaction due to its high exothermicity (1.7 eV), large cross-section (*ca.* 100 Å^2), and lack of an activation barrier.

2. Theory

For many years after the discovery, the true nature of H_3^+ remained a mystery. In a lucid paper using molecular orbital theory, Coulson (1935) predicted the equilibrium structure of H_3^+ to be an equilateral triangle with a bond length of 0.85 Å, quite

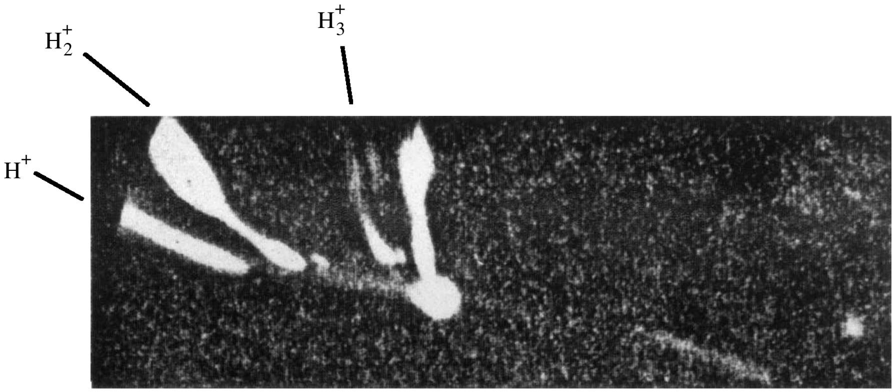

Figure 1. ‘On several plates taken when the discharge-tube contains hydrogen, the existence of a primary line for which $m/e = 3$ has been detected. There can, I think, be little doubt that this line is due to H_3,. . . Above it are lines due to hydrogen atom and molecule. The other lines on the plates are due to the oxygen atom and to the mercury atom. The existence of this substance is interesting from a chemical point of view, as it is not possible to reconcile its existence with the ordinary conceptions about valency, if hydrogen is regarded as always monovalent’ (from Thomson 1912).

close to the modern value of 0.87 Å. In spite of the importance Coulson attached to this work on ‘the simplest molecule’, his prediction was not accepted by Eyring, Hirschfelder and others. Coulson himself does not refer to this prescient paper in his classic book *Valence*. With the advent of computers, however, his prediction was confirmed and the stability of the non-classical three-centre, two-electron bond was established (Christoffersen *et al.* 1964; Conroy 1964). Soon it was evident that H_3^+ has no stable electronically excited states and its only sharp spectrum would be the vibration–rotation spectrum in the infrared. Many *ab initio* theoretical papers have been published on this spectrum, starting from the classic work by Carney & Porter (1976). The variational formalism developed by Sutcliffe & Tennyson (1987) and applied extensively to H_3^+ by Miller & Tennyson (1989) based on the *ab initio* potential of Meyer *et al.* (1986) was essential in understanding the laboratory spectra of hot, overtone and combination bands of H_3^+. In the last decade, the accuracy of the theoretical calculation has increased so much that the small corrections due to adiabatic and relativistic effects have become important (Dinelli *et al.* 1997; Jaquet *et al.* 1998). J. K. G. Watson discusses the theory of vibration–rotation interactions in H_3^+ and recent developments in the field in this issue.

3. Interstellar H_3^+

In the 1930s and 1940s the predominance of hydrogen and the presence of diatomic molecules in interstellar space were established. Martin *et al.* (1961) advocated the high efficiency of reaction (1.1) in producing H_3^+ ‘to the virtual exclusion of H_2^+’, and pointed out the possibility of detecting H_3^+ in interstellar space. Herzberg (1967) considered likewise and stressed that ‘the possibility of detecting H_3^+ in interstellar space depends on the discovery of a spectrum of this molecule in the laboratory’. The science of H_3^+ gained a new dimension when Herbst & Klemperer (1973) and W. D. Watson (1973) published their seminal papers on molecule formation based on cosmic-ray driven ion–neutral reactions. In this scheme, H_3^+ acts as the universal protonator through the proton hop reactions

$$H_3^+ + X \rightarrow HX^+ + H_2, \tag{3.1}$$

which initiate a myriad of chain reactions. Their theory has given a great stimulus to studies of ion–molecule reactions and ion spectroscopy. Recent advances in this field and the major role H_3^+ plays in the scheme are discussed by Herbst in this issue. When $X = HD$ in the above equation, the reaction is slightly exothermic due to the imbalance in the zero point vibrations. This small exothermicity leads to a large deuterium fractionation because of the extremely low temperature of molecular clouds (Watson 1976). Recent advances in this field are discussed by Millar *et al.* in this issue. While the production of interstellar H_3^+ is effected through cosmic-ray ionization of H_2 into H_2^+ followed by reaction (1.1), the destruction may be due to either the proton hop reaction (3.1) (with $X = CO$ and O) or electron recombination, depending on the number density of the medium. This bimodal nature of the destruction mechanism can lead to a bistability of interstellar chemistry, as discussed by Pineau des Forêts & Roueff in this issue.

4. Dissociative recombination

The Langevin rates of reactions (1.1) and (3.1) are well established, but the rate of the electron recombination of H_3^+ is not sufficiently understood. Since the earliest measurement of Leu *et al.* (1973), the experimental value of the rate constant has fluctuated by more than four orders of magnitude. Since the work by Amano (1988), the values determined by several methods seem to be converging to *ca.* $10^7\ \mathrm{cm}^3\ \mathrm{s}^{-1}$, but there are still controversies. Recent experimental results are summarized by Larsson in this issue. Since laboratory experiment cannot be conducted in the same low-density and field-free conditions of interstellar space, it is highly desirable that we have a theoretical understanding of electron recombination to back up the experimental results. The discussion in this issue by Orel *et al.* illustrates the large discrepancy between theory and experiment, which has persisted for several years. The understanding of this process is of primary importance in the astrophysics of H_3^+ and molecular formation. Herein lies an opportunity for theoretical atomic or molecular physics to make a decisive contribution to astrophysics, just as in the case of the opacity of the Sun and H^- (Chandrasekhar & Breen 1946), the isoelectronic sibling of H_3^+.

5. Spectroscopy

In spite of the simplicity of H_3^+, its spectrum defied detection for many years since the initial attempt by Thomson (1913). During the 1920s and 1930s, several papers claimed its detection but they were later shown to be due to H_2 Rydberg states. The detection of H_3^+ had to await the age of laser spectroscopy (Oka 1980). The observed infrared spectrum of the ν_2 fundamental band is shown in figure 2. The spectrum was analysed by J. K. G. Watson using the traditional perturbation treatment of the vibration–rotation interaction (Watson 1984). Since then the spectroscopy of H_3^+ has been greatly extended to hot bands, overtone and combination bands, and forbidden

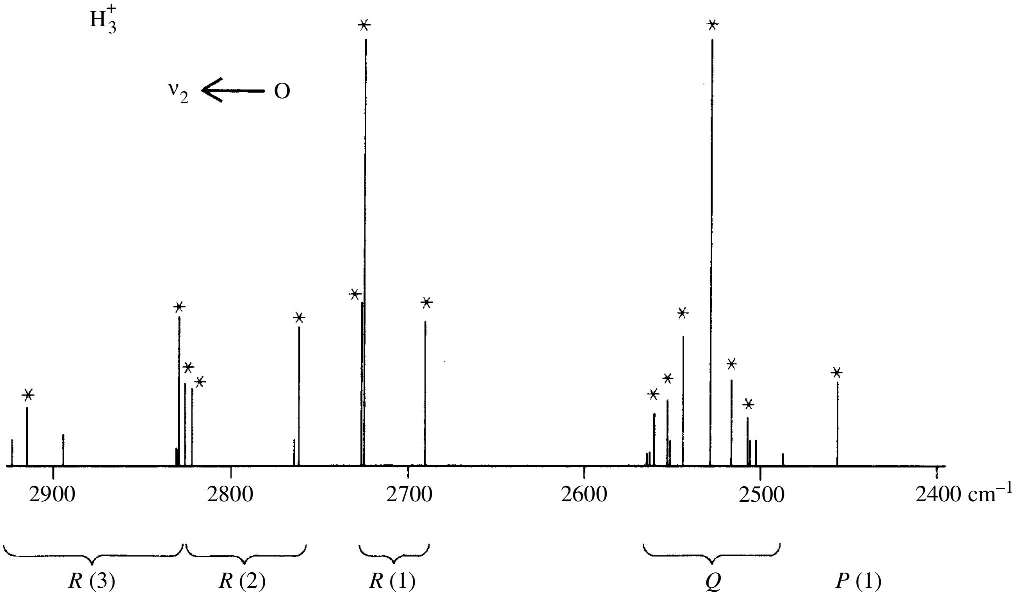

Figure 2. The spectral pattern for the ν_2 band of H_3^+ calculated by Watson for the rotational temperature of 200 K. Observed transitions are marked with asterisks (Oka 1980).

transitions, as discussed by McCall in this issue. Using a very sensitive method of ion-beam predissociation spectroscopy, Carrington *et al.* (1982) observed an extremely rich spectrum of H_3^+ near the dissociation limit, which is yet to be assigned. Recent progress in the experiment and the theory of this spectrum is discussed by Kemp *et al.* and Tennyson *et al.*, respectively, in this issue.

6. H_3^+ emission in planets

A search for interstellar H_3^+ was attempted (Oka 1981) immediately after the discovery of the laboratory spectrum, but its detection had to wait 15 more years. The first non-terrestrial spectrum of H_3^+ came with the serendipitous discovery of the strong overtone emission from the auroral regions of Jupiter (Trafton *et al.* 1989; Drossart *et al.* 1989), which was assigned to H_3^+ by J. K. G. Watson (see Oka (1992) for more detail). The remarkably strong and pure emission of the H_3^+ fundamental band (Maillard *et al.* 1990) is shown in figure 3. This background-free spectrum has allowed planetary scientists to study the morphology and temporal variation of plasma activities in the jovian ionospheres by simply taking images of Jupiter with infrared cameras equipped with a proper filter. The great progress of planetary science made possible by the H_3^+ spectrum is discussed by Connerney & Satoh in this issue. Miller *et al.* speculate (this issue) that not only is H_3^+ a powerful probe but that it also plays a major role in the dynamics of the jovian ionosphere and magnetosphere. The H_3^+ emission has also been observed in Uranus and Saturn and used to study their planetary ionospheres. In the future they may even be observable from giant extra-solar planets, such as those orbiting Tau Bootes.

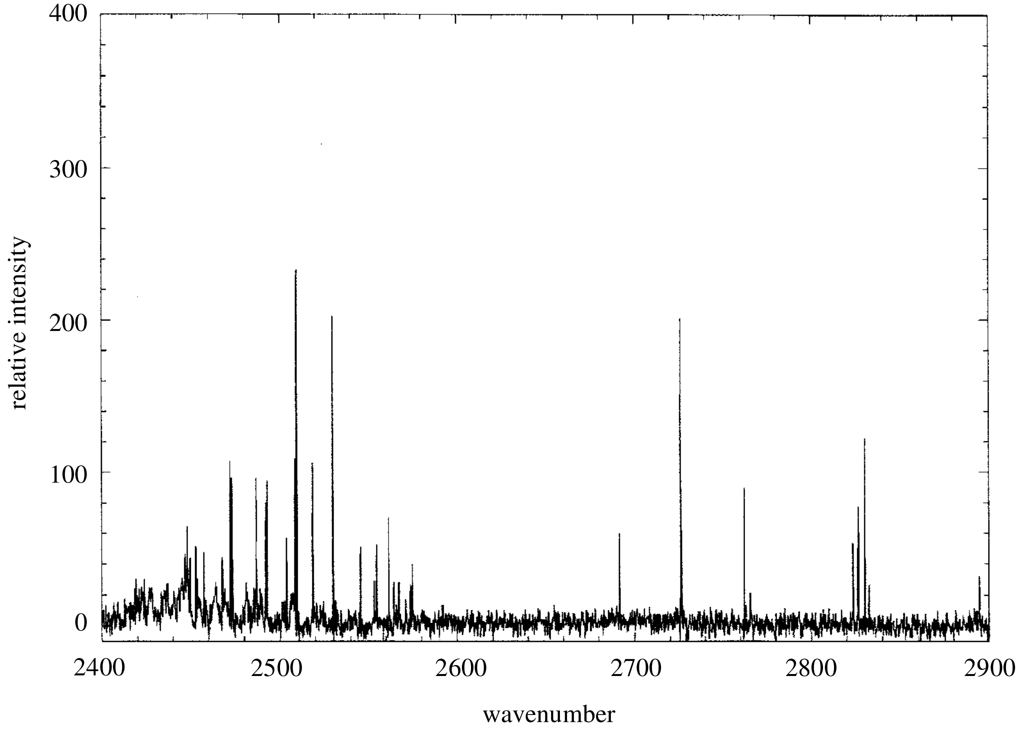

Figure 3. The intense and pure H_3^+ emission spectrum recorded on the southern hemisphere of Jupiter at 60° latitude and mean longitude 40° (Maillard *et al.* 1990).

7. H_3^+ absorption in interstellar space

In the meantime, searches for interstellar H_3^+ continued with negative, inconclusive or false results published by several groups. It was clear that H_3^+ was the most important molecular species yet to be detected. A possible detection of H_3^+ emission in supernova SN1987A was reported (Miller *et al.* 1992). In 1996, the improvement in the sensitivity and operation of the astronomical infrared spectrometer through the use of array detectors finally led to the detection of H_3^+ absorption in molecular clouds (Geballe & Oka 1996). The observed H_3^+ column densities agreed approximately with theoretical expectation, and these observations provided the most direct evidence supporting the cosmic-ray driven ion–neutral reaction scheme for the chemistry of molecular clouds. Subsequently, H_3^+ has also been discovered in the diffuse interstellar medium (McCall *et al.* 1998) with similar column densities as in molecular clouds. This is currently a mystery, since the large relative abundance of electrons in the diffuse interstellar medium makes the expected H_3^+ number density very low because of the large recombination rate. Geballe discusses the observed results and analyses in this issue. Black presents the view that the 'diffuse' environment in which H_3^+ is detected may not be a representative one and also discusses some further topics on interstellar H_3^+. The solution of the enigma of H_3^+ in the diffuse interstellar medium requires the participation of astronomers, physicists and chemists in many fields, which makes this discussion meeting particularly inspiring and timely.

I am indebted to W. A. Lester for drawing my attention to Coulson's work. I thank E. Herbst, S. Miller and J. K. G. Watson, co-organizers of this meeting, and my graduate students C. M. Lindsay and B. J. McCall, for their critical reading of this paper.

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